Modified carbons for enhanced nucleophilic substitution reactions of adsorbed methyl bromide

Hsin-Se Hsieh, Joseph J. Pignatello[*]

Department of Environmental Sciences, The Connecticut Agricultural Experiment Station, 123 Huntington Street, P.O. Box 1106, New Haven, CT, 06504-1106, United States

ABSTRACT

Activated carbons are highly-effective adsorbents for the passive removal of organic pollutants from aqueous and gaseous phases. However, the pollutant remains chemically unchanged and poorly available to dissolved reagents. In this study, we developed quaternary ammonium (QA)-modified carbon adsorbent-catalysts that can catalyze direct reactions between adsorbed molecules and anionic reagents, thereby permitting a trap-and-degrade strategy. The concept was applied to base hydrolysis of methyl bromide (CH_3Br, MeBr), a quarantine and pre-shipment fumigant of concern as an ozone-depleting gas. Modifications of the carbons included irreversible adsorption of the cationic polyelectrolyte, poly (diallyldimethylammonium chloride) (PDADMAC), and covalent grafting of QA groups via precursors (Quat188 and Quab360). In mixtures of the carbon in 1 M NaOH at 55 °C under conditions where hydrolysis in the aqueous phase was negligible, first-order rate constants were increased by up to a factor of 7.4 compared to the unmodified carbon. Combined PDADMAC/Quat188 modification was superior to the corresponding individual modification. Rate acceleration was due to attraction of hydroxide ions to the newly-created anion exchange sites. This is supported by effects of QA modification on anion exchange capacity, point of zero charge, and isoelectric point, as well as by the results of competition experiments with otherwise-inert monovalent anions. The modified catalysts are robust for at least five hydrolysis cycles. QA modification also greatly enhances hydrolysis at unadjusted pH (8.6–10.2) and nucleophilic reaction by thiosulfate. QA modification of carbons is a promising approach for *in situ* trapping and degrading MeBr or other hydrophobic compounds that are reactive toward anionic reagents.

1. Introduction

Methyl bromide (CH_3Br, MeBr) is an effective chemosterilant used in agriculture and international trade [1]. Due to its ozone-depleting potential, MeBr has been banned under the Montreal Protocol, but exemptions exist for quarantine and pre-shipment (QPS) fumigation and other critical uses where suitable alternatives are unavailable [2]. The global consumption of MeBr for QPS has been ~10,000 metric tons per year over the last decade [3]. In typical QPS applications, MeBr is released into a closed chamber containing the target commodity (*e.g.*, timber, produce), and after a period of time the spent MeBr vapor is vented directly into the atmosphere. Because of regulatory pressure on the industry to contain these emissions, there is an urgent need for technologies to capture and/or destroy MeBr from QPS vent streams.

Several approaches have been suggested for the in-line destruction of MeBr. Cerium oxides [4] and ruthenium oxides [5] have been shown to catalyze the combustion of MeBr in simulated QPS vent streams and industrial exhausts, respectively, at temperatures as low as 400 °C. In

solutions containing methyltricaprylammonium chloride as a phase transfer catalyst, MeBr at realistic concentrations was efficiently wet scrubbed and degraded by various sulfur-containing nucleophiles at room temperature [6]. Despite their high efficiency in bench and pilot scale tests, none of these technologies has been widely adopted due to practical obstacles or additional costs including costs associated with the disposal of waste products.

Other strategies for eliminating MeBr emissions from vent streams that have been studied include trap-and-recycle and trap-and-degrade approaches using activated carbon (AC) as the trapping agent. AC can adsorb up to 10% by weight of MeBr from fumigation vent streams at realistic vapor concentrations and humidities [7–9]. Although adsorbed MeBr can be recovered by thermal desorption [10,11], the recovered product typically contains unacceptable levels of moisture and odorous substances from the fumigated commodity. Electrolysis effectively degrades MeBr, but the reaction is slow and organic byproducts have not been characterized [12,13]. MeBr is also subject to S_N2 nucleophilic attack [14]. Peterson et al. [15] reported that coconut shell AC

impregnated with triethylene diamine (TEDA) increased the break-through time due to methylation of TEDA by MeBr, but the reaction is adversely affected by humidity. Gan and Yates reported the decom-position of AC-adsorbed MeBr in a solution of 0.2 M thiosulfate to bromide ion within ~9 h at 20 °C [16], but the reaction seems to be rate-limited by desorption of MeBr [12], and the hazards of the major product, methylthiosulfate, remain unclear.

We recently reported [17] that base hydrolysis of MeBr in AC-aqueous NaOH mixtures occurs in both the aqueous and adsorbed states. At AC-aqueous liquid ratios where the adsorbed state of MeBr is thermodynamically favored (> 95% of total mass present), the rate of MeBr hydrolysis is much greater in the adsorbed state than the dis-solved state. Thus, hydrolysis in AC-aqueous NaOH mixtures is a po-tentially viable trap-and-degrade approach for treating MeBr-laden vent streams. After a detailed mechanistic study it was concluded that anion exchange of hydroxide is a key step in the pathway of hydrolysis oc-curring in the adsorbed state. This was supported by findings that the adsorbed-state hydrolysis rate constant was, a) directly related to the anion exchange capacity (AEC) of the carbon; b) nonlinearly related to the aqueous hydroxide concentration; c) reduced by addition of com-petitive inert anions (nitrate, bromide, perchlorate); and d) increased by the addition of quaternary ammonium surfactants, including cetyl-trimethylammonium and tetrabutylammonium chlorides (CTAC and TBAC, respectively). Carbons normally have few anion exchange sites especially under alkaline conditions. Through that study [17] the pos-sibility that rates could be increased by reversing the surface charge and increasing the AEC by modification of the surface with quaternary ammonium (QA) functional groups became apparent.

Quaternary ammonium compounds (QACs) have been incorporated into ACs for purposes of anion scavenging or anion transport regulation [18–23]. Modification of AC by CTAC increases its adsorption capacity for bromate [20]. Mahmudov et al. [21] found that the removal capa-city for anions, especially perchlorate, was directly related to the chain length of adsorbed *n*-alkyl trimethylammonium. Hou et al. [22] de-monstrated that grafting chlorohydrin-based QACs to AC increased perchlorate breakthrough bed volume. Wang et al. [23] demonstrated that anchoring QA groups to ACs significantly improves their efficiency as air cathodes in microbial fuel cells (MFCs) by promoting OH$^-$ flux within pores. In contrast to the above-mentioned purposes, QA mod-ification of ACs for increasing *in-situ* degradation of AC-adsorbed con-taminants has received no attention.

There are many instances that would benefit from the use of an adsorbent-catalyst that could concentrate the target compound from the aqueous or gaseous phase and catalyze its degradation in situ ('trap-and-degrade' approach). The treatment of QPS vent streams containing MeBr is one such instance because MeBr is poorly soluble in aqueous reagent solutions, yet is highly effectively adsorbed by carbons [7–9]. In one example using this approach, the MeBr vent stream could be passed through a bed of AC that is continuously bathed in a spray of alkaline liquid. In this study, we investigated the effects of in-corporating QA groups into carbons on nucleophilic reactions of ad-sorbates with anionic reagents. It was expected that incorporation of QA groups would reduce negative surface charge and increase the anion exchange affinity for the attacking nucleophile without seriously re-ducing target compound adsorption. Although CTAC and TBAC accel-erate base hydrolysis of adsorbed MeBr [17], their use is not very practical since they adsorb reversibly [24] and have some inherent toxicity [25]. Instead we turned to other, less reversible incorporation techniques: non-covalent adsorption of a cationic polyelectrolyte and covalent grafting of chlorohydrin-based QACs. We hypothesize the ca-tionic polyelectrolyte will attach at multiple points along the surface by associating electrostatically with carboxyl/hydroxyl groups; hence, its adsorption will be irreversible. At the same time, we expect its ad-sorption to provide excess positive charge that will increase anion ex-change capacity for hydroxide. The covalent grafting of chlorohydrin-based QACs to hydroxyl groups is a well-established technique, and the

resulting anion exchange capacity thus introduced should remain stable over regenerative processes. The effects of surface modification on physical-chemical properties of the ACs and MeBr degradation rate were evaluated. The reusability of the surface-modified ACs was also studied.

2. Materials and methods

2.1. Materials

WPX powdered activated carbon (325 mesh) was received from Calgon Carbon (Moon Township, PA). Norit RO 0.8 activated carbon pellet was purchased from Sigma Aldrich (Milwaukee, WI). Poly(dia-llyldimethylammonium chloride) solution (PDADMAC; average MW < 100,000, 35 wt.% in H$_2$O), Toluidine blue O, poly(vinyl sulfate) potassium salt, and sodium perchlorate (98%) were purchased from Sigma Aldrich. Sodium hydroxide pellet (98%), potassium hydroxide pellet (86%), sodium bromide (99%), ethyl acetate (99.9%), sodium tetraphenylborate (99%), tetrabromophenolphthalein ethyl ester po-tassium salt were purchased from Fisher Scientific (Pittsburgh, PA); (3-chloro-2-hydroxypropyl) trimethylammonium chloride solution (Quat188, 65 wt.% in H$_2$O) was from TCI America (Portland, OR); (3-chloro-2-hydroxypropyl) cocoalkyl dimethylammonium chloride solu-tion (Quab360, 38 wt.% in H$_2$O) was from SKW QUAB Chemical (Saddle Brook, NJ); and sodium nitrate (ACS grade) was from Mallinckrodt (St. Louis, MO). Aqueous solutions were prepared with water purified by a Millipore Milli-Q Integral 10 system.

2.2. Preparation of carbons

The PDADMAC-coated ACs were prepared by mixing 5 g AC with 16 g of the 35 wt.% PDADMAC solution and 16 mL water in a 40 mL polypropylene (PP) centrifuge tube and equilibrating on a tube rotator at room temperature for 24 h to allow PDADMAC to adsorb. Afterward, the supernate was removed and the ACs were washed with four 30 mL portions of water to remove non- and loosely-bound PDADMAC. This was followed by anion exchange, first with sodium bromide (0.5 M and 0.1 M in sequence) and then with potassium hydroxide (0.5 M twice). Each step took 30 min on a tube rotator. Treatment with NaBr removed residual chloride ion to prevent formation of methyl chloride, an un-wanted byproduct. Treatment with KOH removed bromide which may inhibit base hydrolysis (see Section 3.3). Following anion exchange, the modified ACs were rinsed with ten 30 mL portions of water and dried at 65 °C for 48 h.

The QA-grafted ACs were prepared by methods in Hou et al. [22]. AC (5 g) was first mixed with 20 mL of as-received solutions of the chlorohydrin-based QACs (Quat188 or Quab360) on a tube rotator for 24 h to adsorb the compounds. Epoxidation was commenced by adding 10 mL water and enough NaOH pellet (corresponding to about 0.12–0.15 mole) to raise the pH to 13.5 and the mixture was heated at 50 °C for 48 h. The reaction that takes place on the surface may be written (using Quat188 as an example),

.
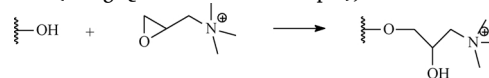
The non-grafted QACs and byproducts from aqueous epoxide reac-tions were removed by four sequential washes with 15 ml alcoholic mixture (90% ethanol, 5% methanol, 5% 2-propanol) alternating with 30 mL water. Effective grafting of QA to carbons by this procedure has been verified previously by X-ray photoelectron spectroscopy (XPS) [22,23]. Following grafting, anion exchange was carried out in the same way as for PDADMAC-coated ACs. To prepare ACs incorporated with both PDADMAC coating and QA grafting, the ACs were first grafted and washed as above, and then treated with PDADMAC, anion exchanged, rinsed, and dried as above.

Batch leaching tests with water were performed on PDADMAC-,

Quat188-, and Quab360-modified ACs. In addition, the sorption-desorption isotherm of PDADMAC was determined on RO pellets. The methods for leaching, construction of the isotherm, and methods of analysis for PDADMAC [26], Quat188, and Quab360 are described in the Supplementary Information section.

2.3. Characterization of modified ACs

2.3.1. BET surface area

Surface area and porosity were measured by N_2 adsorption on a Quantachrome Autosorb-1C after outgassing at 105 °C to pass the instrument criterion. The 11-point Brunauer–Emmett–Teller specific surface area (SSA_{BET}) was measured in the pressure range P/P_0 of 0.05–0.3 and the total pore volume (V_{total}) was measured at P/P_0 of 0.995.

2.3.2. Adsorption of MeBr

Pure MeBr gas collected *via* a Tedlar sampling bag was injected through the PTFE-lined silicone septum into 8.8 mL vials containing AC and 2 mL of water. After equilibrating at room temperature (~ 20 °C) for 2 h with gentle mixing, 30 µL of the headspace was withdrawn by gastight syringe and injected directly into a gas chromatograph (see Section 2.4.3). The aqueous concentration was calculated from the dimensionless Henry's law constant ($K_H = 0.264$ L_{aq}/L_{air}) determined previously [17]. The amount of AC-adsorbed MeBr was then calculated by subtracting the amounts of MeBr remaining in the headspace and aqueous phase from the injected amount. Sorption isotherms were fit to the Freundlich model,

$$C_{AC} = K_F C_{aq}^N \tag{1}$$

where K_F and N are the Freundlich adsorption and linearity coefficients, and C_{AC} and C_{aq}, respectively, represent the adsorbed and aqueous MeBr concentrations.

2.3.3. Anion exchange capacity

The measurement of anion exchange capacity (AEC) of ACs was modified from a standard method used for soil samples [27]. Air-dried AC (0.5 g) was first saturated with bromide by equilibrating with 10 mL of 1 M NaBr in a 15 mL PP centrifuge tube on a tube rotator for 24 h. After centrifugation and removal of supernate, the sample was washed five times with 10 mL portions of 0.01 M NaBr. The final wash mixture was adjusted to pH 9 $\pm$ 0.2 by NaOH or HCl and allowed to equilibrate for 12 h. After centrifugation, bromide concentration (C_1) was determined in the separated supernatant phase. The tubes were then weighed to determine the entrained solution volume (V_1). Perchlorate rather than nitrate was used to exchange bromide for determining the AEC because it has a greater ion selectivity coefficient on QA sorbents [28]. The adsorbed bromide was exchanged four times with 8 mL portions of 0.5 M NaClO$_4$. Each exchange included the steps of shaking by hand for 1 min, equilibration on a tube rotator for 1 h, centrifugation, and separation of the supernate by pipette and passing through a 0.45 µm Nylon filter. The known combined volume of supernate (V_2) was used for determining bromide concentration (C_2). The AEC is calculated by,

$$AEC \,(mol\,kg^{-1}) = (C_2 V_2 - C_1 V_1)/W_{AC} \tag{2}$$

where W_{AC} is the mass of AC. Bromide was determined by bromide selective electrode (Cole-Parmer). Perchlorate was maintained at the same concentration in samples and calibration standards. Nevertheless, preliminary tests indicated no interference by perchlorate up to 0.1 M.

2.3.4. Zeta potential and mass titration

Zeta potential was measured by Dynamic Light Scattering technique on a Malvern Zetasizer (Nano-ZS90). Suspensions were prepared by mixing 0.05 g WPX with 125 mL water. After vigorous shaking by hand, 10 mL aliquots were dispensed into 22 mL glass tubes and dosed with

NaOH or HCl to pH values spanning the range 2.5–13.5. After 12 h equilibration, zeta potential was measured twice on duplicate 1 mL subsamples. The isoelectric point (pH_{IEP}) was taken as the pH where the zeta potential was zero. The point of zero charge (PZC) of the ACs was determined by mass titration [29], and the average value of the three asymptotic pH values was taken as the pH_{PZC}.

2.4. Degradation of adsorbed MeBr

2.4.1. Degradation kinetics

For kinetics studies, pure MeBr gas (1.5 mL, ~ 5.5 mg) was injected through the septum of replicate 5 mL vials containing 0.5 g AC. After equilibration at room temperature for 30 min, the vials were chilled at -20 °C for at least 30 min. The degradation of MeBr was initiated by pipetting 1 mL aqueous solution into the vials and replacing the septum. The vials were then placed in a constant temperature chamber. Duplicate vials were removed at predetermined times and chilled at -20 °C for at least 30 min before adding 2 mL of ethyl acetate to extract the remaining MeBr from both the aqueous and solid phases. Extraction was done by vortex-mixing for 5 min and followed by centrifugation for 2 min. The ethyl acetate extraction recovery of MeBr from as-received WPX was 73.6 $\pm$ 1%.

2.4.2. Recycling of modified ACs

Replicate samples of RO pellets (5.5 g) were subjected to m hydrolysis cycles ($m \leq 4$) before measuring the degradation rate in the ($m + 1$)th cycle. Each cycle included a) pre-adsorption of 60 mL pure MeBr (~ 4% by weight) on the AC; b) addition of 1 M NaOH (11 mL); c) hydrolysis at 55 °C for 3 h; and d) discarding the supernate and washing the solid with three 30 mL portions of water. The solid was washed two more times with 30 mL portions of water and dried at 105 °C for 8 h prior to measuring the rate.

2.4.3. Sample analysis

Headspace samples or ethyl acetate extracts (after pre-filtering through a 0.2 µm Nylon filter) were analyzed by injection onto a GS-Q PLOT column (30 m × 0.535 mm) in an Agilent gas chromatograph equipped with a flame ionization detector (GC-FID) with 20 mL min^{-1} H$_2$ as carrier gas. The inlet temperature was 150 °C and detector temperature was 300 °C. The oven temperature was initially 100 °C, where it was held for 6 min. The temperature was then ramped to 200 °C at 40 °C/min, where it was held for 3 min. Calibration curves were constructed by injecting MeBr into empty vials (for headspace samples) or into 2 mL ethyl acetate.

3. Results and discussion

3.1. Surface area and sorption isotherms

Table 1 lists pore and surface properties of as-received and modified WPX and RO carbons. Both total porosity (V_{total}) and specific surface area (SSA_{BET}) decrease along the series: as-received > Quat188-grafted > PDADMAC-coated > Quab360-grafted material. The lower values for Quab360 compared to Quat188 may be attributed to the greater hydrocarbon chain length in the former (cocoalkyl *vs* propyl, respectively). Long chains may plug pores, limiting access to N_2 [30]. In addition, Quab360 is more strongly adsorbed for solvophobic reasons, and thus may graft more efficiently to the carbon.

Fig. 1 shows the adsorption isotherms of MeBr on the as-received and modified carbons together with their Freundlich log K_F and N values. As expected, a decrease in surface area due to surface modification results in a decrease in adsorption capacity for MeBr. The log K_F value follows the same order as the SSA_{BET}: as-received (3.23) > Quat188-grafted (3.01) > PDADMAC-coated (2.99) > Quab360-grafted (2.73). This is true also for the distribution ratio ($K_d = C_{AC}/C_{aq}$, L/kg) calculated at constant MeBr concentration of 9000 mg kg^{-1}: as-received

Table 1
Selected physicochemical properties of as-received and modified carbons.

	SSA_{BET}[a] (m^2/g)	V_{total}[b] (cm^3/g)	AEC[c] $(\mu mol/g)$	pH_{pzc}[d]	pH_{IEP}[d]
Calgon WPX					
As-received	754	0.54	94.4 ± 0.7	9.68	5.80
PDADMAC-coated	557	0.43	335.6 ± 1.6	10.14	> 13.3
Quat188-grafted	626	0.45	131.7 ± 2.5	9.78	6.91
Quab360-grafted	103	0.18	174.9 ± 4.2	10.15	7.90
Norit RO 0.8					
As-received	849	0.65	113.7 ± 0.6	9.49	–
PDADMAC-coated	478	0.41	420.0 ± 10.9	9.94	–
Quat188-grafted	583	0.49	202.1 ± 9.5	9.66	–
Quab360-grafted	114	0.20	$218.9 \pm .9.1$	10.20	–

[a] SSA_{BET} = specific surface area determined with the 11-point BET method.
[b] V_{total} = total pore volume measured at $P/P_0 = 0.995$.
[c] Anion exchange capacity at pH = 9 ± 0.2.
[d] pH_{pzc} by mass titration method. pH_{IEP} from the zeta potential measurement.
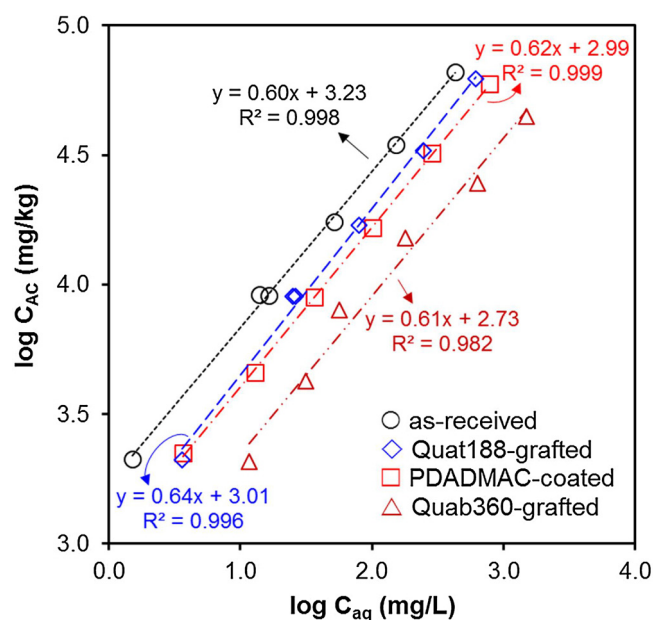

Fig. 1. Sorption isotherms of MeBr to as-received and surface modified WPX from aqueous solution at 20 °C. The dotted lines represent Freundlich model fits, with the slope (*x* coefficient) and intercept in each case equaling *N* and log K_F, respectively.

(558) > Quat188-grafted (301) > PDADMAC-coated (256) > Quab360-grafted (89).

3.2. Anion exchange capacity and surface charge

Table 1 lists surface charge properties of as-received and modified WPX and RO carbons. Zeta potential as a function of pH is shown in Fig. 2 for WPX carbons. Coating with PDADMAC greatly increased the AEC (335.6 and 420 μmol/g-AC, respectively) compared to the as-received carbons (94.4 and 113.7 μmol/g-AC, respectively). In addition, the zeta potential-pH curve of PDADMAC-coated WPX increased relative to the as-received WPX and was displaced into the positive region over the entire pH range. Thus, binding of PDADMAC both neutralizes carboxyl/hydroxyl functional groups and introduces excess positive charge. Being an electrokinetic parameter, zeta potential reflects charge mainly on external surfaces.

Grafting ACs with Quat188 or Quab360 also substantially increased
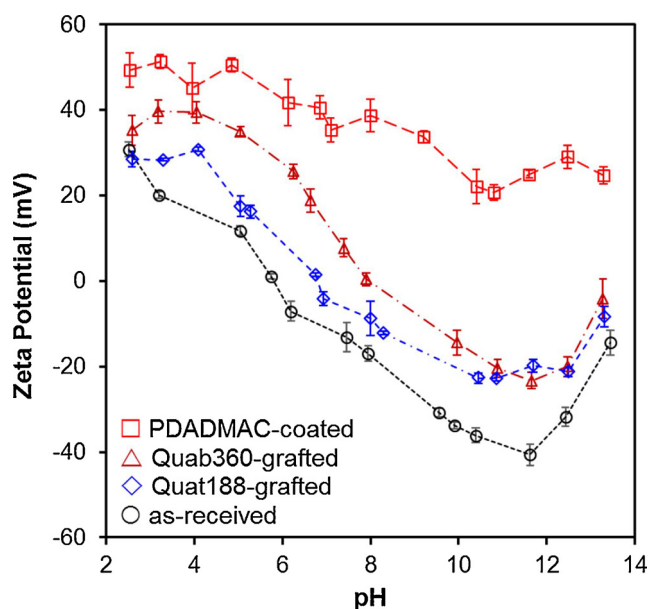
Fig. 2. Zeta potential of as-received and modified WPX carbons as a function of pH. Ionic strength was uncontrolled, possibly explaining the inversion of zeta potential above pH 12 for all carbons.

the AEC (Table 1) and zeta potential (Fig. 2) relative to the as-received carbons. Moreover, grafting of WPX with these reagents generally increased the pH_{IEP}. Quab360 appears to be more efficiently grafted than Quat188 to both WPX and RO, considering the consistently greater AEC, greater zeta potential, and lower SSA_{BET} of the grafted carbons

The pH_{PZC}, which is determined by titration, reflects the contributions of both external and internal charge within the micropore (< 2 nm) and mesopore (2–50 nm; IUPAC definitions) systems (hereafter, nanopore systems). The pH_{PZC} values are listed in Table 1 and the titration plots are provided in Figs. S1 and S2. As-received WPX and RO carbons were alkaline, with pH_{PZC} values of 9.68 and 9.49, respectively. Introduction of QA groups generally increased pH_{PZC}, along the order: Quab360-grafted ~ PDADMAC-coated > Quat188-grafted > as-received. The difference between pH_{PZC} and pH_{IEP} ($\Delta pH_{PZC-IEP}$) of a modified AC relative to that of the as-received AC (3.88) reflects the degree to which the introduced charge was placed in internal pore surfaces as opposed to external surfaces. The $\Delta pH_{PZC-IEP}$ of PDADMAC-WPX (< −3.16) indicates that most of the introduced charge was placed externally, as expected from its great size relative to most pore sizes. By contrast, the values of $\Delta pH_{PZC-IEP}$ for Quat188-WPX (2.87) and Quab360-WPX (2.25) in comparison to as-received WPX (3.88) indicate that considerably more of the introduced positive charge was placed internally. The values also indicate that more of the introduced positive charge was placed externally for Quab360-WPX than for Quat188-WPX, which is in line with the greater steric bulk of Quab360 relative to Quat188. The desired condition for carbon-mediated base hydrolysis may be internal placement of charge, where most of the adsorbed MeBr molecules likely reside.

3.3. Base hydrolysis of MeBr

The hydrolysis rate law for MeBr can be expressed as [17],

$$-\frac{dM_{tot}}{dt} = k_{obs,tot}M_{tot} = \{k_{obs,aq} \cdot f_{aq} + k_{obs,AC} \cdot f_{AC}\}M_{tot} \quad (3)$$

where M_{tot} is the total spiked amount in the reaction vessel; $k_{obs,tot}$ is the overall pseudo first-order rate constant (h^{-1}); $k_{obs,aq}$ and $k_{obs,AC}$ are the observed pseudo first-order rate constants (h^{-1}); and f_{aq} and f_{AC} are the mass fractions, of MeBr in the aqueous and adsorbed phases, respectively. Incorporated in the terms $k_{obs,aq}$ and $k_{obs,AC}$ is the hydroxide
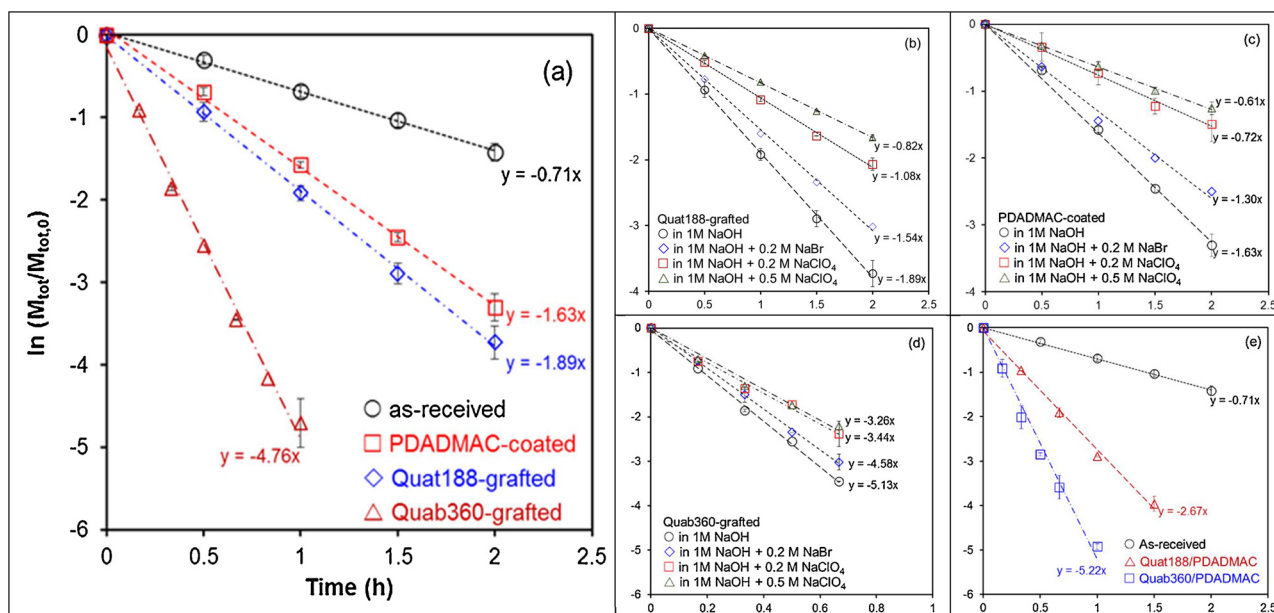
Fig. 3. Rates of base hydrolysis of adsorbed MeBr on as-received or modified WPX carbons at 55 °C (0.5 g of carbon, 1 mL of 1 M NaOH) under conditions of predominant adsorptive phase reaction. (a) Effect of surface modification. (b–d) Effect of added perchlorate and bromide ions. (e) Combined surface modification effect of PDADMAC coating and QA grafting. All plots share same axis labels. Aqueous hydrolysis in the absence of AC was reported elsewhere [17].

ion concentration in the respective phase.

Base hydrolysis of MeBr was conducted at 55 °C at initial adsorbed concentration of 11 mg/g and a ratio of 1 M NaOH solution to AC of 2 mL g^{-1}. It is noted that 55 °C was chosen for the purpose of demonstration. Rates at other temperatures may be calculated on the basis of the activation energy, E_a, for base hydrolysis on carbons. In the previous study [17] the E_a for base hydrolysis of MeBr in the adsorbed state on cetyltrimethylammonium-coated WPX (53.8 ± 1.1 kJ/mol) was found to be 10.3 kJ/mol lower than that on the pristine carbon, suggesting that the QA coating stabilizes the transition state in some way. Fig. 3a shows the temporal trends of total MeBr remaining in the vessel for as-received and surface-modified WPX. The reaction is pseudo first-order in MeBr concentration. Table 2 lists the rate constants and fractions in each phase calculated on the basis of the isotherms in Fig. 1. Under the conditions, MeBr is mostly (> 92%) sorbed. Knowing the rate constant for aqueous base hydrolysis in 1 M NaOH determined previously ($k_{obs,aq}$ = 6.8 ± 0.4 h^{-1}) [17] allows calculation of the contribution of hydrolysis in the adsorbed state as a fraction of total hydrolysis—*i.e.*, the ratio, $f_{AC} \cdot k_{obs,AC}/k_{obs,tot}$. It can be seen that hydrolysis occurs predominantly (> 96%) in the adsorbed state for all carbons despite the fact that the pseudo first-order rate constant for the aqueous phase is higher than that for the solid phase. This is a consequence of highly favorable partitioning of MeBr to the carbon.

It is further seen that PDADMAC coating and QA grafting accelerate hydrolysis. Relative to as-received WPX, $k_{obs,tot}$ increased by 570% for Quab360-, 166% for Quat188-, and 130% for PDADMAC-modified WPX. The larger $k_{obs,tot}$ for Quab360-WPX compared to Quat188-WPX reflects the greater AEC, pH$_{PZC}$, and pH$_{IEP}$ of Quab360-WPX, and supports the hypothesis that introduction of grafted QA groups increases the availability of OH$^-$ to sorbed MeBr by providing anion exchange sites.

The anion exchange mechanism is further supported by the effects of added inert anions, which may compete with OH$^-$ for positively charged sites. Fig. 3b–d show that addition of NaBr or NaClO$_4$ to Quat188-, Quab360-, or PDADMAC-modified ACs retards MeBr hydrolysis in the order, 0.5 M NaClO$_4$ > 0.2 M NaClO$_4$ > 0.2 M NaBr. Fig. S3 shows the same trend for the as-received WPX. The order between perchlorate and bromide is the same as the order in their ion selectivity coefficients on quaternary ammonium anion exchange resins [28]. We showed previously that the selected inert anions added individually do not react with MeBr, nor do they affect the aqueous hydrolysis rate constant [17].

PDADMAC coating also enhances hydrolysis, but less so than Quab360 and Quat188 grafts, even though it has the largest AEC and the most positive zeta potentials across the pH scale among the modified carbons. Fig. 3d shows that the catalytic effect of PDADMAC
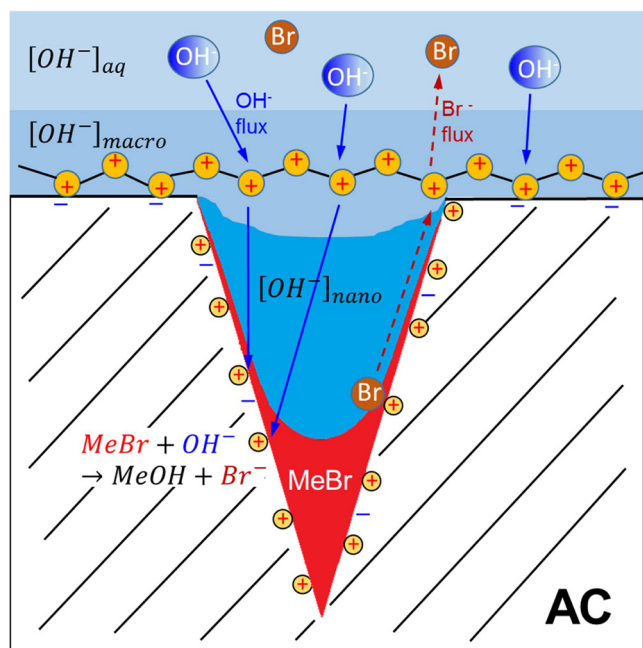
Table 2
Pseudo first-order rate constants and fractions of MeBr in adsorbed and aqueous states for base hydrolysis of MeBr in the presence of WPX from the experiments in Fig. 3a.

	$k_{obs,tot}$[a] (h^{-1})	f_{aq}[b]	f_{AC}[b]	$f_{aq} \cdot k_{obs,aq}$[c] (h^{-1})	$k_{obs,AC}$[d] (h^{-1})	$f_{AC} \cdot k_{obs,AC}/k_{obs,tot}$
As-received	0.71 (0.02)	0.0040 (0.0005)	0.987 (0.001)	0.027 (0.004)	0.69 (0.02)	0.96 (0.04)
Quat188-grafted	1.89 (0.02)	0.0072 (0.0019)	0.978 (0.004)	0.049 (0.013)	1.89 (0.03)	0.97 (0.02)
Quab360-grafted	4.76 (0.16)	0.0227 (0.0167)	0.929 (0.038)	0.154 (0.114)	4.97 (0.29)	0.97 (0.05)
PDADMAC-coated	1.63 (0.02)	0.0089 (0.0001)	0.972 (< 0.001)	0.060 (0.004)	1.62 (0.02)	0.96 (0.02)

Number in parentheses is the standard error after propagation of errors.
[a] Overall pseudo first-order rate constant calculated from data in Fig. 3a.
[b] Fractions of MeBr in aqueous solution and AC, calculated from the sorption isotherms in Fig. 1 by using Henry's law constant (K_H) of 0.601 L$_{aq}$/L$_{air}$ [17] to account for partitioning into the headspace.
[c] Using $k_{obs,aq}$ of 6.8 ± 0.4 h^{-1} in 1 M NaOH solution from a previous study [17].
[d] $k_{obs,AC}$ = ($k_{obs,tot}$ − $f_{aq} k_{obs,aq}$)/f_{AC}.

Fig. 4. Mechanism showing how PDADMAC coating and Quat188 or Quab360 grafting catalyze the base hydrolysis of AC-adsorbed MeBr. Arrows represent flux of reagent (OH$^-$) and produced (Br$^-$) anions. Blue colors indicate OH$^-$ in regions with different concentration (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

coating is completely negated by addition of 0.2 M NaClO$_4$ (*i.e.*, the $k_{obs,tot}$ was approximately equal to that of the as-received WPX), whereas this was not the case for Quat188 and Quab360. This result suggests that PDADMAC-introduced anion exchange sites are more accessible to competing anions. A reasonable explanation, as illustrated in Fig. 4, is that PDADMAC resides mainly in macropores and on external surfaces of AC due to its enormous size, whereas Quat188 and Quab360 QA groups reside mainly in nanopores, where most of the surface area lies and where most MeBr molecules reside.

An expression for the total ion-exchanged hydroxide concentration on the AC may be written,

$$[OH^-]_{AC} = [OH^-]_{macro} + [OH^-]_{nano} = (K_{macro\text{-}aq} + K_{nano\text{-}aq})[OH^-]_{aq} \quad (4)$$

where $[OH^-]_{macro}$, $[OH^-]_{nano}$, and $[OH^-]_{aq}$ are the hydroxide ion concentrations in/on macropores/external surfaces, in nanopores, and in the bulk solution, respectively, and $K_{macro\text{-}aq}$ and $K_{nano\text{-}aq}$ are the coefficients of hydroxide ion partitioning between the macropore/external surface and nanopore regions, respectively, and the bulk solution. Eq. (4) suggests that the hydrolysis of adsorbed MeBr can be promoted by increasing the hydroxide ion in macropores/external surfaces (*i.e.*, PDADMAC coating), or in nanopores (*i.e.*, QAC grafting), or both. If the distribution of MeBr in macropores/external surfaces and nanopores is considered, the total hydrolysis in adsorbed state can be further expressed as,

$$k_{obs,AC} \cdot f_{AC} = k_{AC} \cdot [OH^-]_{macro} \cdot f_{macro} + k_{AC} \cdot [OH^-]_{nano} \cdot f_{nano} \quad (5)$$

where f_{macro} and f_{nano} are the mass fractions of MeBr in/on macropores/external surfaces and in nanopores, respectively. In highly MeBr-laden ACs, f_{nano} is expected to be much greater than f_{macro} due to the effect of capillary condensation. This may explain why PDADMAC-coated AC has higher AEC but gives lower rate enhancement than those grafted with Quat188 and Quab360.

To test the hypothesis further, we examined the degradation of MeBr by ACs modified by combinations of QA grafting and PDADMAC

coating (Fig. 3e). The addition of PDADMAC coating increased the AEC of Quat188-WPX from 131.7 μmol/g to 402.2 μmol/g, and increased the AEC of Quab360-WPX from 174.9 μmol/g to 243.3 μmol/g. A possible explanation for the weaker increase of AEC for Quab360-WPX is that, since Quab360 grafts better on external surfaces than does Quat188, there are fewer carboxyl/hydroxyl sites on the external surfaces of Quab360-WPX available to provide anchoring sites for PDADMAC. The addition of PDADMAC coating increased the $k_{obs,tot}$ for Quat188-WPX from 1.89 h^{-1} to 2.67 h^{-1}, and the $k_{obs,tot}$ for Quab360-WPX from 4.76 h^{-1} to 5.22 h^{-1}. Thus, combined modifications produce more effective hydrolysis catalysts than the corresponding individual modifications, but the effect is not additive. Compared to the as-received WPX, combined PDADMAC/Quab360-WPX modification gives a rate enhancement of nearly an order of magnitude.

3.4. Hydrolysis of MeBr without added base

QA modification also enhances hydrolysis of adsorbed MeBr under conditions closer to neutral. Reactions were run at the unadjusted pH of the AC-water mixture, which ranged from 8.6 to 10.2 depending on the sample. For dissolved MeBr within this pH range, H$_2$O is a more important nucleophile than OH$^-$ due to concentration effects: i.e., at 55 °C the "neutral" hydrolysis rate constant k_{H2O} (H$_2$O as the nucleophile) is 7.2×10^{-2} h^{-1} [32], whereas the base hydrolysis rate constant $k_{obs,aq}$ at pH 10 (OH$^-$ as the nucleophile) calculated from its value in 1 M NaOH [17] is 6.8×10^{-4} h^{-1}. Fig. 5 shows that the $k_{obs,tot}$ for the as-received WPX at the natural pH of 10 is 0.077 $\pm$ 0.003 h^{-1}. Knowing f_{aq} from Fig. 1 (0.0040 $\pm$ 0.0005), $k_{obs,tot}$ is much greater than the combined neutral and base hydrolysis rate constants for the aqueous phase: $f_{aq}(k_{H2O} + k_{obs,aq}) = (2.9 \pm 0.4) \times 10^{-4}$ h^{-1}.

Fig. 5 further shows that QA modification results in an increase in $k_{obs,tot}$ to 0.27 h^{-1} for PDADMAC-WPX, 0.24 h^{-1} for Quat188-WPX, and 1.47 h^{-1} for Quab360-WPX. Thus, QA modification accelerates hydrolysis up to a factor of 19 in this pH range under our conditions. The contributions of hydrolysis in the two phases are detailed in Table S1 for these systems. Just like base hydrolysis, nearly all hydrolysis in this lower pH range can be attributed to reaction in the adsorbed state (*i.e.*, $f_{AC} \cdot k_{obs,AC}/k_{obs,tot} \geq 93.5\%$). Fig. S4 shows kinetic experiments with added 0.2 M NaClO$_4$ under same conditions. After comparison
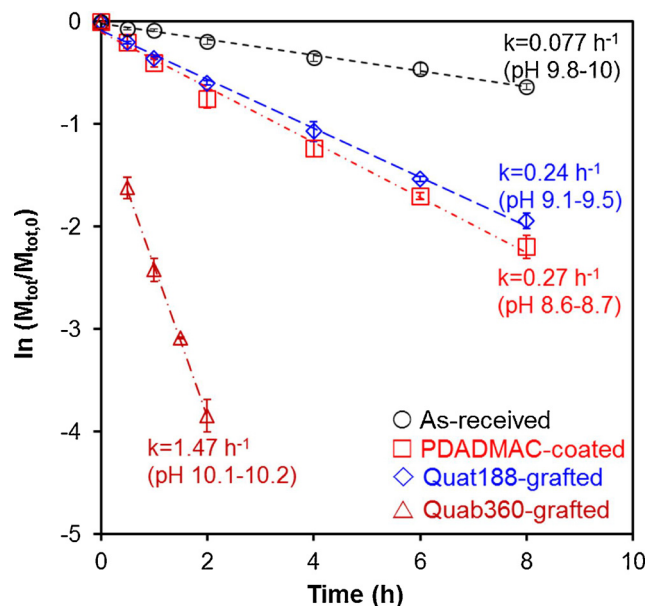

Fig. 5. Rates of water hydrolysis of adsorbed MeBr on as-received or modified WPX carbons at 55 °C and a water/solid ratio of 2 mL g^{-1}. The pH was measured after 1 h equilibration at room temperature in separate vessels at the same water/solid ratio but on larger scale.

with Fig. 5, it is clearly seen that $NaClO_4$ inhibits hydrolysis of adsorbed MeBr in both the as-received and QA-modified carbons. This is strong evidence that catalytic activity of the QA coatings toward hydrolysis, even in the lower pH range, is due to concentration of OH^- from the aqueous phase to the AC surface.

From the results of this study it is clear that the introduction of anion exchange sites *via* PDADMAC coating or QA grafting accelerates base hydrolysis of MeBr over a wide pH range.

3.5. Nucleophilic substitution by thiosulfate

Thiosulfate ($S_2O_3^{2-}$) is a much stronger nucleophile than OH^- toward MeBr [31]. A previous study found that the rate of thiosulfate reaction with AC-adsorbed MeBr was only slightly dependent on the aqueous thiosulfate concentration [12]. This may have been due to the limited anion exchange capacity of the AC used, forcing the reaction to occur in the aqueous phase, and making desorption rate-limiting. We regarded it possible that introduction of QA functional groups onto AC could increase the rate by increasing the AEC and decreasing electrostatic repulsion of thiosulfate.

Fig. 6 shows that 0.1 M thiosulfate reacts with pre-adsorbed MeBr in a first order manner, with $k_{obs,tot}$ for as-received WPX equal to $0.52\,h^{-1}$ at 25 °C, similar to the reported value of 0.3–$0.5\,h^{-1}$ between 0.003 M and 0.03 M thiosulfate [12]. Modification of WPX with PDADMAC, Quat188, or Quab360 increases the $k_{obs,tot}$ by a factor of about 4, with Quat188 being slightly more effective, and PDADMAC being slightly less effective than Quab360. Note that the first-order plots for PDADMAC-WPX and Quab360-WPX do not intersect zero, indicating that their reactions decelerate at some point during the first quarter hour. At this time we do not have a clear explanation for that behavior. The results show that QA modification can accelerate thiosulfate degradation of adsorbed MeBr, presumably by increasing anion exchange capacity.

3.6. Reusability of modified ACs

To test catalyst stability of the modified carbons with respect to base hydrolysis of AC-adsorbed MeBr, we compared the $k_{obs,tot}$ of as-received and modified RO pellets after each of several cycles. The pellets were washed between cycles. Fig. 7 shows that the activity of the as-received RO was unchanged after five cycles. The activity of the modified
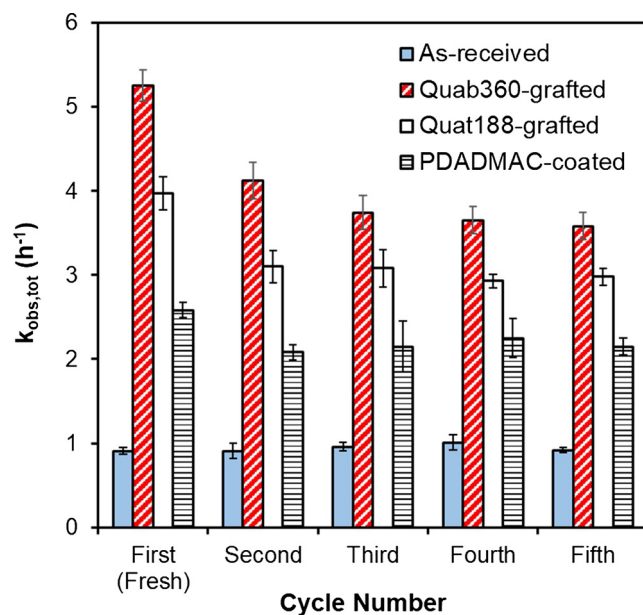
Fig. 7. Pseudo first-order degradation rate constants for base hydrolysis of MeBr adsorbed to RO pellets after successive cycles at 55 °C. Ratio of 1 M NaOH solution to carbon, $2\,mL\,g^{-1}$.

carbons declined by about 20% between the first (fresh) and second cycles, but then remained practically unchanged over the additional three cycles. The decrease in activity between the first and second cycles may be due in part to occupancy of some anion exchange sites by Br^- produced in the first cycle, or to leaching of non-grafted or non-adsorbed QA units. With respect to the grafted units, tests showed leaching of some Quat188 (but not Quab360) after the first leaching cycle (Fig. S5). The leached residues may have been entrained inside pores or between the particles during the respective synthesis procedure.

Of particular interest is the reversibility of PDADMAC coating, since it is not covalently attached. The sorption isotherm of PDADMAC on Norit RO pellets on log scale (Fig. 8) is biphasic, with an abrupt change to lower slope occurring at ~1 mg/mL. The upper phase then rises slightly exponentially with further increase in concentration. The distribution ratio, K_d, is $213\,mL\,g^{-1}$ at the lowest tested concentration (0.0037 mg/mL), decreasing to $0.58\,mL\,g^{-1}$ at the highest (176 mg/mL). In the low concentration range, sorption is driven predominantly by electrostatic attraction of the QA groups of PDADMAC with (predominantly external) negatively charged surface carboxyl and hydroxyl groups. When most of the negatively charged sites are neutralized, further sorption reverses the net charge, and sorption affinity becomes reduced due to electrostatic repulsion and solvation of the units. To test reversibility, desorption isotherms were constructed starting from three different adsorbed concentrations. No significant desorption occurred, despite a reduction in the aqueous-phase concentration of at least 2.5 orders of magnitude. Moreover, the PDADMAC concentration in the leachate from successive aqueous washings showed that the leachate concentration was reduced quickly to < 0.005 mg/mL (see SI and Fig. S6). These results indicate that PDADMAC adsorption is largely irreversible, which is encouraging from the standpoint of catalyst stability, catalyst reusability, and the disposal of aqueous wastes from MeBr treatment.

3.7. Conclusions and implications

Adsorbent-catalysts that can effectively concentrate contaminants from the fluid phase, while catalyzing their breakdown *in situ* are highly desirable in many situations. In this study, we have demonstrated that
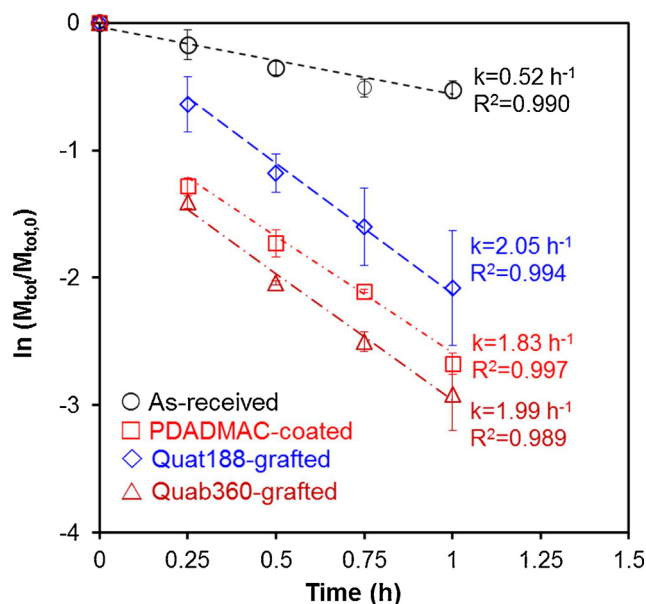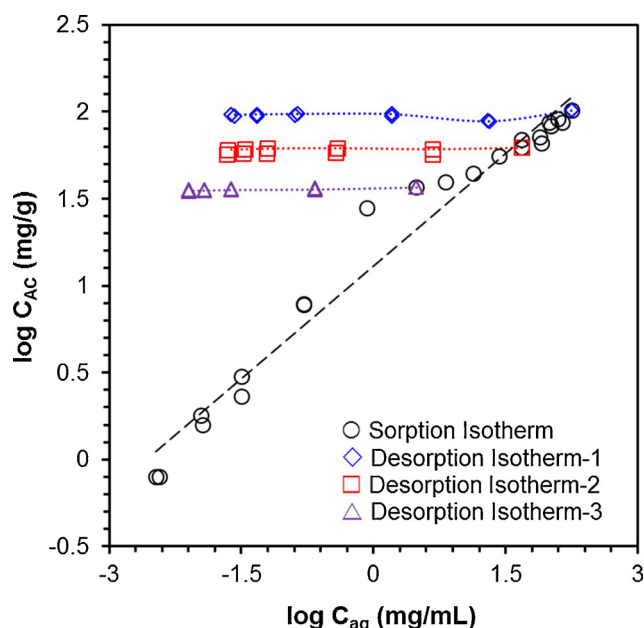
Fig. 6. Rates of reaction of thiosulfate with adsorbed MeBr on as-received or modified WPX carbons at 25 °C (0.5 g carbon, 1 mL of 0.1 M $Na_2S_2O_3$).

Fig. 8. Sorption-desorption isotherms of PDADMAC to Norit RO pellets at 25 °C. The pH was uncontrolled. The dashed line represents the Freundlich model fit to the sorption branch. The dotted lines connect the data points of each desorption branch to the respective origin on the sorption branch. The starting points for three desorption isotherms (36.8, 62.2, and 102 mg/g-AC) are revealed by the overlapping colored data points.

base hydrolysis of AC-adsorbed MeBr can be enhanced by incorporating QA groups into carbons. While ACs effectively remove and concentrate MeBr from the gas and/or aqueous phases, the QA groups attract hydroxide ions from surrounding reagents to the carbon interface where they attack adsorbed MeBr molecules. Under conditions of nearly complete adsorption, hydrolysis takes place predominantly in the adsorbed state. Coating of the cationic polyelectrolyte PDADMAC increases hydroxide partitioning in macropores and external surface regions, whereas and grafting of the QACs, Quat188 or Quab360, increases hydroxide partitioning primarily into nanoporous regions, making the combination of coating and grafting with these reagents an attractive strategy. MeBr hydrolysis is accelerated over a wide pH range, which is encouraging from a practical standpoint. The $k_{obs,tot}$ at pH 10.1 is only 3.5-times smaller than at pH 14 (1 M NaOH), but 19 times greater than the as-received carbon. Thus, it may be possible to use a lower concentration of NaOH in the AC-suspended scrubber to remove MeBr. The modified carbons do not lose activity after several cycles. Lastly, because the rate of adsorbed MeBr degraded by thiosulfate was also enhanced, this study shows that QA modification may be a means to accelerate other reactions between adsorbed compounds and anionic reagents.

Acknowledgement

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.apcatb.2018.04.007.

References

[1] J.B. Ristaino, W. Thomas, Agriculture, methyl bromide, and the ozone hole: can we fill the gaps? Plant Dis. 81 (1997) 964–977.
[2] U.S. Environmental Protection Agency, Exemption for methyl bromide, https://www.epa.gov/ods-phaseout/methyl-bromide (Accessed 14 July 2017).
[3] M. Pizano, I. Porter, M. Besri, Report of the Methyl Bromide Technical Options Committee, United Nations Environment Programme, 2015. Ozone Secretariat, 2014.
[4] C.-Y. Chen, J.J. Pignatello, Catalytic oxidation for elimination of methyl bromide fumigation emissions using ceria-based catalysts, Appl. Catal. B: Environ. 142–143 (2013) 785–794.
[5] X. Liu, J. Zeng, J. Wang, W. Shi, T. Zhu, Catalytic oxidation of methyl bromide using ruthenium-based catalysts, Catal. Sci. Technol. 6 (2016) 4337–4344.
[6] R. Bielski, P.J. Joyce, The use of methyltricaprylylammonium chloride as a phase transfer catalyst for the destruction of methyl bromide in air streams, Org. Process Res. Dev. 12 (2008) 781–784.
[7] J.G. Leesch, G.F. Knapp, B.E. Mackey, Methyl bromide adsorption on activated carbon to control emissions from commodity fumigations, J. Stored Prod. Res. 36 (2000) 65–74.
[8] J. Gan, N.E. Megonnell, S.R. Yates, Adsorption and catalytic decomposition of methyl bromide and methyl iodide on activated carbons, Atmos. Environ. 35 (2001) 941–947.
[9] J.P. Wood, M.J. Clayton, T. McArthur, S.D. Serre, L. Mickelsen, A. Touati, Capture of methyl bromide emissions with activated carbon following the fumigation of a small building contaminated with a Bacillus anthracis spore simulant, J. Air Waste Manage. Assoc. 65 (2015) 145–153.
[10] K. Miura, A. Nakanishi, K. Hashimoto, Treatment of the poisonous gas remaining after fumigation by use of an activated carbon adsorber, Ind. Eng. Chem. Process Des. Dev. 22 (1983) 469–477.
[11] J.D. Snyder, J.G. Leesch, Methyl bromide recovery on activated carbon with repeated adsorption and electrothermal regeneration, Ind. Eng. Chem. Res. 40 (2001) 2925–2933.
[12] Y. Yang, Y. Li, S.S. Walse, W.A. Mitch, Destruction of methyl bromide sorbed to activated carbon by thiosulfate or electrolysis, Environ. Sci. Technol. 49 (2015) 4515–4521.
[13] Y. Li, C. Liu, Y. Cui, S.S. Walse, R. Olver, D. Zilberman, W.A. Mitch, Development of an activated carbon-based electrode for the capture and rapid electrolytic reductive debromination of methyl bromide from postharvest fumigations, Environ. Sci. Technol. 50 (2016) 11200–11208.
[14] A. Streitwieser, Solvolytic displacement reactions at saturated carbon atoms, Chem. Rev. 56 (1956) 571–752.
[15] G.W. Peterson, J.A. Rossin, P.B. Smith, G.W. Wagner, Effects of water on the removal of methyl bromide using triethylene diamine impregnated carbon, Carbon 48 (2010) 81–88.
[16] J. Gan, S.R. Yates, Recapturing and decomposing methyl bromide in fumigation effluents, J. Hazard. Mater. 57 (1998) 249–258.
[17] H.-S. Hsieh, J.J. Pignatello, Activated carbon-mediated base hydrolysis of alkyl bromides, Appl. Catal. B: Environ. 211 (2017) 68–78.
[18] A. Bhatnagar, W. Hogland, M. Marques, M. Sillanpää, An overview of the modification methods of activated carbon for its water treatment applications, Chem. Eng. J. 219 (2013) 499–511.
[19] C.Y. Yin, M.K. Aroua, W.M.A.W. Daud, Review of modifications of activated carbon for enhancing contaminant uptakes from aqueous solutions, Sep. Purif. Technol. 52 (2007) 403–415.
[20] W.-f. Chen, Z.-Y. Zhang, Q. Li, H.-Y. Wang, Adsorption of bromate and competition from oxyanions on cationic surfactant-modified granular activated carbon (GAC), Chem. Eng. J. 203 (2012) 319–325.
[21] R. Mahmudov, C. Chen, C.-P. Huang, Functionalized activated carbon for the adsorptive removal of perchlorate from water solutions, Front. Chem. Sci. Eng. 9 (2015) 194–208.
[22] P. Hou, F.S. Cannon, N.R. Brown, T. Byrne, X. Gu, C.N. Delgado, Granular activated carbon anchored with quaternary ammonium/epoxide-forming compounds to enhance perchlorate removal from groundwater, Carbon 53 (2013) 197–207.
[23] X. Wang, C. Feng, N. Ding, Q. Zhang, N. Li, X. Li, Y. Zhang, Q. Zhou, Accelerated OH– transport in activated carbon air cathode by modification of quaternary ammonium for microbial fuel cells, Environ. Sci. Technol. 48 (2014) 4191–4198.
[24] R. Parette, F.S. Cannon, The removal of perchlorate from groundwater by activated carbon tailored with cationic surfactants, Water Res. 39 (2005) 4020–4028.
[25] K. Nakata, T. Tsuchido, Y. Matsumura, Antimicrobial cationic surfactant, cetyltrimethylammonium bromide, induces superoxide stress in Escherichia coli cells, J. Appl. Microbiol. 110 (2011) 568–579.
[26] B. Gumbi, J.C. Ngila, P.G. Ndungu, Direct spectrophotometric detection of the endpoint in metachromatic titration of polydiallyldimethylammonium chloride in water, Phys. Chem. Earth, Parts A/B/C 67–69 (2014) 117–124.
[27] L.W. Zelazny, L. He, A. Vanwormhoudt, D.L. Sparks, A.L. Page, P.A. Helmke, R.H. Loeppert (Eds.), Methods of Soil Analysis Part 3—chemical Methods, Soil Science Society of America, American Society of Agronomy, Madison, WI, 1996, pp. 1231–1253.
[28] H.P. Gregor, J. Belle, R.A. Marcus, Studies on ion-exchange resins. XIII. Selectivity coefficients of quaternary base anion-exchange resins toward univalent anions, J. Am. Chem. Soc. 77 (1955) 2713–2719.
[29] J.S. Noh, J.A. Schwarz, Effect of HNO3 treatment on the surface acidity of activated carbons, Carbon 28 (1990) 675–682.
[30] K.S.W. Sing, F. Rouquerol, J. Rouquerol, P. Llewellyn, Adsorption by Powders and Porous Solids: Principles, Methodology and Applications, second ed., Academic Press, Oxford, 2014.
[31] R.P.G. Schwarzenbach, M. Philip, Dieter M. Imboden, Environmental Organic Chemistry, second ed., John Wiley & Sons, Inc., 2002.
[32] W. Mabey, T. Mill, Critical review of hydrolysis of organic compounds in water under environmental conditions, J. Phys. Chem. Ref. Data 7 (1978) 383–415.